

Effect of Isovalent Substitution of Bi Cations by La Cations on the Crystal Structure and Thermodynamic Properties of Nanocomposites Based on Bismuth Ferrite

V.B. Dolgoshey^{1,*}, O.M. Fesenko², T.V. Tsebriinko², A.V. Klochek², S.M. Ponomarenko¹,
A.V. Semchenko³, V.V. Sidsky³

¹ NTUU "KPI named after Igor Sikorsky", 37, Peremohy Ave, 03056 Kyiv, Ukraine

² Institute of Physics of the NAS of Ukraine, 46, Prospect Nauki, 03039 Kyiv, Ukraine

³ Francisk Skorina Gomel State University, 104, Sovetskaya St., 246019 Gomel, Belarus

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The work is devoted to the study of nanocomposites of bismuth ferrites (BFO) and bismuth lanthanum ferrites (BLFO). The effect of substitution of Bi cations by La cations on the crystal structure and thermodynamic properties of bismuth ferrites was studied. These composites were prepared by the modern method of sol-gel synthesis. Scanning electron microscope (SEM) images of the prepared samples were obtained. Using SEM method, it was established that the morphology of BFO and BLFO is similar. All samples have a granular microstructure with granule sizes from 20 to 100 nm. This means that, at a scale above 200 nm, all samples are morphologically indistinguishable, while structural features appear at smaller scale levels. X-ray diffraction analysis was performed, and the thermodynamic properties of these bismuth ferrites were studied. X-ray diffraction study revealed the crystallinity of bismuth ferrites at a scale level of less than one nanometer. It was found that the formation of nanocomposites based on bismuth ferrites occurs according to the nucleation mechanism of non-isothermal crystallization. When cooled, the BFO sample is a three-component material. As a result of the substitution of La cations for Bi cations, a more homogeneous two-component BLFO structure is formed, which consists of BiLaFeO₃ crystallites and Bi₂Fe₄O₉ crystallites with approximately equal dimensions (about 0.400 nm³). It was also found a decrease in the heat capacity, enthalpy, entropy and Gibbs energy modulus in BLFO compared to BFO, which indicates an improvement in the thermodynamic compatibility of components due to a decrease in heat losses at structural defects.

Keywords: Bismuth ferrites, Lanthanum, Crystallinity, Thermodynamic properties, Heterogeneity.

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1. INTRODUCTION

The most unique properties of bismuth ferrites are their high magnetic and electrical characteristics at room temperature [1]. Nowadays, to improve the ferroelectric and magnetoelectric behavior of nanocomposites based on bismuth ferrites, the effects of replacing Bi cations with cations of other rare-earth elements with a close ion radius, similar type and size of crystallites, etc. are widely studied.

According to statistical thermodynamics, the maximum degree of packing of crystallites is achieved using chemical elements with different atomic radii [2]. This leads to minimum configurational entropy, configurational enthalpy, and configurational Gibbs free energy for arbitrary melts of multicomponent materials. Therefore, it is quite logical that substitution of Bi cations by cations of other rare-earth metals can greatly improve the properties of bismuth ferrites [3].

In accordance with the principles of nonequilibrium chemical thermodynamics, it is energetically advantageous to replace a chemical element with an element with a smaller atomic radius and/or with a lower atomic weight [4]. Therefore, it will be efficient to replace Bi cations (standard atomic weight 209) with isovalent La cations (standard atomic weight 139) in BiFeO₃-based nanocomposites. Thus, in recent years, much attention has been paid to the effects of such a replacement.

In our previous work, it was found that an increase in the annealing temperature from 600 to 700 °C

makes it possible to improve the structural organization of bismuth ferrite, since with an increase in thermal mobility, bismuth cations are able to fill defective vacancies in bismuth ferrite crystallites [5]. It was also discovered that the formation of bismuth ferrite by cooling from the melt occurs according to the nucleation mechanism and further non-isothermal crystallization. The main idea of this work was to add a small number of La cations to bismuth ferrite as nucleation centers for further crystallization.

This paper presents studies of the effect of doping bismuth ferrite with a small number of La cations on the crystal structure and thermodynamic properties of nanocomposites based on BiFeO₃.

2. OBJECTS OF STUDY AND EXPERIMENTAL METHODS

2.1 Objects of Study

The objects of research were samples of bismuth ferrite (BFO) and bismuth ferrite doped with 7 wt. % lanthanum cations – (Bi_{0.93}La_{0.07})(FeO₃) (BLFO). The samples were synthesized by the sol-gel method, isothermal annealing at a temperature of 600 °C for 1 h, followed by non-isothermal crystallization upon cooling to room temperature.

To obtain the samples, the following reagents were used: bismuth nitrate pentahydrate Bi(NO₃)₃ × 5H₂O, iron nitrate nanohydrate Fe(NO₃)₃ × 9H₂O, lanthanum

* vdolgoshey@ukr.net

nitrate $\text{La}(\text{NO}_3)_3$, diluted lemon acid $\text{C}_6\text{H}_8\text{O}_7$, and glycerol $\text{C}_3\text{H}_8\text{O}_3$.

The mixture of the total solution was prepared by mixing the solution of $\text{Bi}(\text{NO}_3)_3$ (dissolved in deionized water and in lemon acid $\text{C}_6\text{H}_8\text{O}_7$) and $\text{Fe}(\text{NO}_3)_3$ (dissolved in deionized water). Lanthanum nitrate $\text{La}(\text{NO}_3)_3$ (dissolved in deionized water) was then added and magnetically stirred at room temperature until a clear solution was obtained, after which glycerol was added to the mixture in the required stoichiometry. The resulting gel was then heated in an oven at a temperature of 180°C for 2 h to remove residual water. The mixture was then heated until all solvents were removed. Further, the obtained substance was annealed to a muffle furnace at a temperature of 600°C for 1 h.

2.2 Experimental Methods

SEM/EDS analysis was carried out in high vacuum using a JEOL JSM 6490LV scanning electron microscope (SEM) coupled with an Oxford INCA energy dispersive spectroscopy (EDS) system, comprising Oxford INCA PentaFETx3 Si(Li) detector and INCA Energy 350 processing software, at 20 kV accelerating voltage, spot size 50, and 10 mm working distance.

X-ray diffraction data were obtained in 2θ scattering range from 10.04 to 100° , with a step of 0.04° , on an Ulnima4 diffractometer (Ridaku Americas Corporation (USA), CuK α radiation, wavelength $\lambda = 1.54 \text{ \AA}$). X-ray structural analysis and distribution of components in the samples were carried out using internal software and databases of the Ulnima4.

The study of heat capacity and thermodynamic analysis in the temperature range from 40 to 100°C were carried out using a calorimetric module, which is described in detail earlier [6, 7].

3. RESULTS AND DISCUSSION

SEM images of the studied samples are shown in Fig. 2 on two scales.

From Fig. 2, it can be seen that the morphology of BFO and BLFO is similar. All samples have a granular microstructure with granule sizes from 20 to 100 nm. To study a smaller scale structure, we investigated the nanocrystallinity of the samples by the method of XRD diffraction.

3.1 X-ray Diffraction Study

X-ray diffraction data for BFO and BLFO were obtained in the same 2θ scattering range from 10.04 to 100° with the same step of 0.04° on the diffractometer Ulnima4 (Fig. 3).

X-ray structural analysis and distribution of components in samples were carried out using internal software and databases of Ulnima4. This program was used to identify each peak in X-ray scattering curves and to determine the averaged crystallite parameters (see Table 1).

Three types of crystallites can be seen on the BFO X-ray scattering curve (Fig. 3a). These are peaks at small scattering angles corresponding to BiFeO_3 crystallites, which are characterized by the largest averaged volume

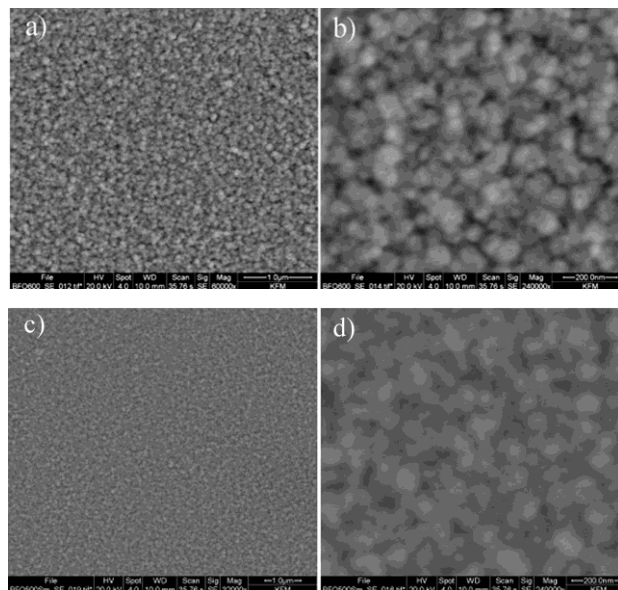


Fig. 2 – SEM images of BFO (a, b) BLFO (c, d)

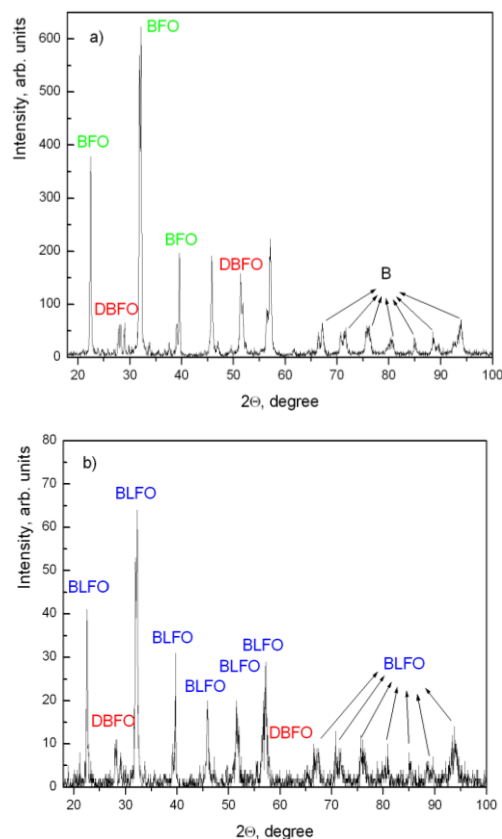


Fig. 3 – Experimental curves of X-ray structural data for the studied samples. BiFeO_3 is marked as BFO, $\text{Bi}_2\text{Fe}_4\text{O}_9$ is marked as DBFO, bismuth is marked as B, and BiLaFeO_3 is marked as BLFO

of the crystal lattice (Table 1), peaks at scattering angles 2θ from 32 to 56° , corresponding to $\text{Bi}_2\text{Fe}_4\text{O}_9$ crystallites with a smaller volume of the crystal lattice (Table 1) and peaks from bismuth crystallites with the smallest crystallite sizes.

The level of X-ray scattering for BLFO sample is much lower than for the initial one (see the scale along

the ordinate in Fig. 3b). For this sample, we found only two types of crystallites corresponding to BiLaFeO₃ and Bi₂Fe₄O₉, respectively. Moreover, it was found that the average volume of BiLaFeO₃ crystallites is slightly lower than the average volume of BFeO₃ (Table 1) as a result of the thermodynamically favorable substitution of bismuth cations by lanthanum cations with a smaller ionic radius [4, 8, 9].

According to the fundamental theories of X-ray scat-

tering on density fluctuations [10, 11], the total intensity of X-ray scattering on a sample is proportional to its heterogeneity and can be calculated from Fig. 3 as:

$$I_{total} = \sum_{2\theta=10,04}^{100} I(2\theta),$$

where $I(2\theta)$ is the intensity of X-ray scattering at each scattering angle.

Table 1 – Parameters of the average crystals lattices

Phase name	n^*	a (nm)	b (nm)	c (nm)	α (deg.)	β (deg.)	γ (deg.)	Volume, (mn ³)	Crystal systems (syngonia)
BFO sample									
BiFeO ₃	18	0.57	0.57	1.39	90.0	90.0	120.0	0.452	hexagonal
Bi ₂ Fe ₄ O ₉	14	0.79	0.84	0.60	90.0	90.0	90.0	0.398	rhombohedral
Bismuth	14	0.47	0.47	0.47	90.0	90.0	90.0	0.104	rhombohedral
BLFO sample									
BiLaFeO ₃	15	0.56	0.56	1.38	90.0	90.0	120.0	0.432	hexagonal
Bi ₂ Fe ₄ O ₉	11	0.79	0.84	0.60	90.0	90.0	90.0	0.398	rhombohedral

* number of peaks

From a brief analysis of the obtained X-ray scattering data, the following conclusions can be drawn.

1. The BFO sample is structurally heterogeneous and is characterized by three types of crystallites: BiFeO₃ crystallites, Bi₂Fe₄O₉ crystallites and residual bismuth crystallites.

2. BiFeO₃ crystallites correspond to the most intensive peaks (see Fig. 3a).

3. Bi₂Fe₄O₉ crystallites are characterized by peaks of lower intensity.

4. The smallest residual bismuth crystallites with dimensions from 0.1 to 0.24 nm correspond to scattering angles 2θ of more than 60 °.

5. The addition of lanthanum cations leads to a significant decrease in the inhomogeneity of nanopowders, probably due to the filling of structural defects with La cations in BiFeO₃ crystals and/or the replacement of Bi cations by La cations (Fig. 3b).

3.2 Thermodynamic Properties

To analyze the thermodynamic properties of samples, the specific heat was determined as:

$$C_p = \frac{(dQ/dT)}{m} = \frac{(dQ/dT)}{\rho \cdot V}, \quad (1)$$

where dQ/dT is the relative heat flow measured using the calorimetric module [12], m is the sample weight, ρ is the sample density, V is the sample volume.

The total heat during heating of the material is equal to the sum of the heat spent to increase its temperature $dQ_{heating}$ and the heat loss dQ_{loss} due to the presence of structural defects in the material [13]:

$$dQ = dQ_{heating} + dQ_{loss}. \quad (2)$$

Measurements of the specific heat capacity of the samples were carried out in the same temperature range for the convenience and correctness of the further analysis (Fig. 5).

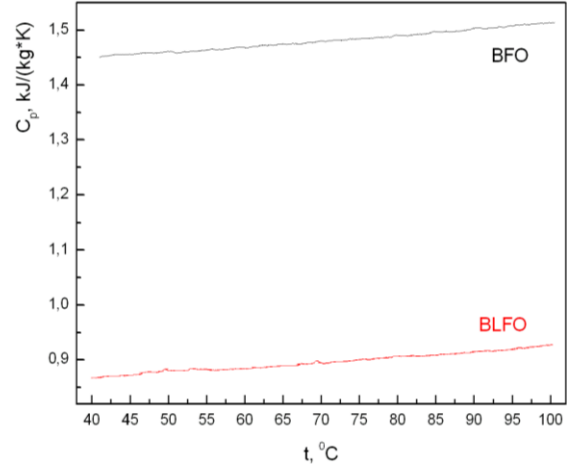


Fig. 5 – Temperature dependences of the specific heat capacity of the studied samples

A significant decrease in the heat capacity of the BLFO sample relatively to BFO indicates an improvement in the crystal structure due to an increase in the packing density of crystallites that leads to an increase in the sample density (see the increase in the denominator in equation (1)) and also due to a decrease in heat losses at structural defects (see equation (2)).

The change in the enthalpy of the thermodynamic system ΔH during heating from temperature T_1 to temperature T_2 was calculated by the following equation [13, 14]:

$$\Delta H(T_1 \rightarrow T_2) = \int_{T_1}^{T_2} C_p(T) dT. \quad (3)$$

The temperature dependences of the change in the enthalpy of the studied samples are shown in Fig. 6.

Lower enthalpy values of BLFO relative to BFO mean lower heat losses dQ_{loss} at structural defects in the samples.

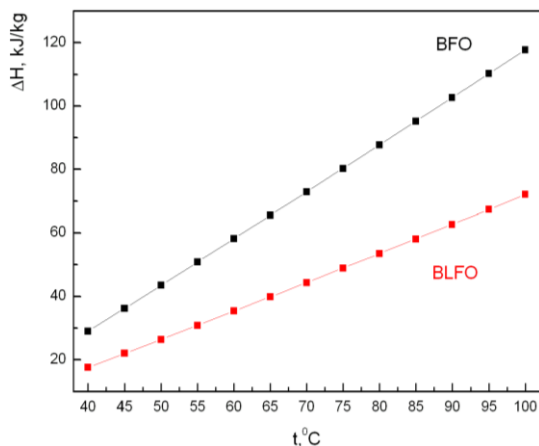


Fig. 6 – Temperature dependences of the enthalpy of the studied samples

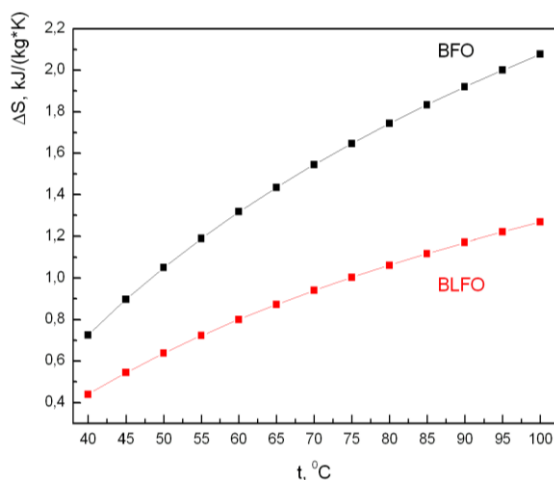


Fig. 7 – Temperature dependences of the entropy of the studied samples

The change in the entropy was found as [14]:

$$\Delta S_{T_i} = \Delta H_{T_i} / T_i. \quad (4)$$

The entropy of BFO is higher than the entropy of BLFO (Fig. 7). From a thermodynamic point of view, this means that the BLFO structure is more ordered.

The change in free energy (or Gibbs energy) (G) was determined as follows [14]:

$$\Delta G_{T_i} = \Delta H_{T_i} - T_i \cdot \Delta S_{T_i}. \quad (5)$$

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As can be seen from equation (5), the change in free energy (ΔG) is determined by two components: the change in enthalpy ΔH , which corresponds to heat loss, and the change in entropy ΔS , which corresponds to a change in mobility. Fig. 8 shows that $\Delta G_{BLFO} > \Delta G_{BFO}$, meaning that after the replacement of bismuth cations by lanthanum cations, heat losses become lower compared to the change in the mobility of structural elements.

In our opinion, the thermodynamic properties of samples mainly depend on the scattering of thermal phonons by density fluctuations [15, 16].

i) a significant decrease in the heat capacity, enthalpy, and entropy modulus of the Gibbs energy of BLFO compared to BFO indicates a decrease in heat losses at structural defects;

ii) higher values of free energy in BLFO mean lower heat losses due to the scattering of thermal phonons at structural defects than in BFO.

There is reason to expect that such a spatial structure will provide a high level of magnetic properties of the obtained samples.

4. CONCLUSIONS

Thus, on the basis of the performed studies, it was found that the formation of nanocomposites based on bismuth ferrite occurs according to the incipient mechanism of non-isothermal crystallization. Upon cooling from the annealing temperature of the BFO sample, a three-component material with a high degree of inhomogeneity is formed. Moreover, the largest BiFeO_3 crystallites have an average size of about 0.450 nm^3 , $\text{Bi}_2\text{Fe}_4\text{O}_9$ crystallites have a size of about 0.400 nm^3 , and the smallest bismuth crystallites have a size of about 0.100 nm^3 .

As a result of the substitution of La cations for Bi cations, a more homogeneous two-component structure BLFO is formed, which consists of BiLaFeO_3 and $\text{Bi}_2\text{Fe}_4\text{O}_9$ crystallites with approximately equal dimensions (about 0.400 nm^3).

It was also found a decrease in the heat capacity, enthalpy, entropy and the Gibbs energy modulus in BLFO compared to BFO, which indicates an improvement in the thermodynamic compatibility of the components due to a decrease in heat losses at structural defects.

There is reason to expect that BLFO samples will have better electromagnetic properties than BFO, since all components contain ferromagnetic groups Fe_2O_4 and Fe_4O_9 .

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Вплив ізовалентного заміщення катіонів Ві на катіони Ла на термодинамічні властивості та кристалічну структуру нанокompatитів на основі BiFeO_3

Володимир Долгошей¹, Олена Фесенко², Тамара Цебриєнко², Анастасія Клочек²,
Сергій Пономаренко¹, Аліна Семченко³, Віталій Сідський³

¹ Національний технічний університет України «Київський політехнічний інститут імені Ігоря Сікорського», Проспект Перемоги, 37, 03056 Київ, Україна

² Інститут фізики НАН України, Відділ міжнародної наукової та інноваційної діяльності, трансферу технологій та захисту інтелектуальної власності, Проспект Науки, 46, 03039 Київ, Україна

³ Гомельський державний університет імені Франциска Скорини, вул. Радянська, 104, 246019 Гомель, Білорусь

Робота присвячена вивченню нанокompatитів вісмут феритів (BFO) та вісмут лантан феритів (BLFO). Досліджено вплив заміщення катіонів Ві катіонами Ла на кристалічну структуру та термодинамічні властивості феритів вісмуту. Дані композити отримані з допомогою сучасного методу золь-гель синтезу. З допомогою скануючої електронної мікроскопії (SEM) було вивчено морфологію нанокompatитів. За даними скануючої електронної мікроскопії зразки BFO і BLFO виявилися подібними. Всі зразки мали зернисту структуру з розмірами зерен від 20 до 100 нм. Це означає, що в масштабі, більшому за 200 нм, всі зразки морфологічно нерозрізнені, а їх структурні особливості проявляються на рівнях меншого масштабу. Одночасно для дослідження кристалічної структури та вивчення теплофізичних властивостей були проведені рентгеноструктурний аналіз та диференціальна скануюча калориметрія. З допомогою рентгеноструктурного аналізу було показано наявність кристалітів з розмірами меншими за 1 нм. Встановлено, що зародження кристалів нанокompatитів на основі вісмут фериту відбувається за механізмом неізотермічної кристалізації. При охолодженні зразка BFO утворюються кристаліти трьох типів. В результаті заміщення катіонів Ві на катіони Ла утворюється більш однорідна, двокомпонентна структура BLFO, що містить кристали BiLaFeO_3 та $\text{Bi}_2\text{Fe}_4\text{O}_9$ з об'ємом близько $0,400 \text{ nm}^3$. Також виявлено зниження питомої теплоємності, ентальпії, ентропії та енергії Гіббса для зразків BLFO. Така поведінка термодинамічних параметрів вказує на поліпшення сумісності компонентів у композитах BLFO завдяки зменшенню структурних дефектів.

Ключові слова: Ферити вісмуту, Лантан, Кристалічність, Термодинамічні властивості, Неоднорідність.